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One major outcome of the workshop was the description of several paths of research that may lead to the production of fullerene nanotubes in large quantities. Of these the most ambitious, but almost certainly also the most rewarding was one that came to be called the "Royal Road." The beginning of this road is the production of small amounts (grams) of single walled fullerene nanotubes from one of the current methods. The road progresses by developing methods to purify this material, and then to cut these tubes into short pieces. These pieces are then used effectively as seed crystals from which to grow fullerene nanotubes continuously from a hydrocarbon feed gas with the help of a catalyst particle attached at the "living" end. This path of fullerene nanotube research is the "Royal" road because it requires the development of the high science and technology of manipulating individual fullerene nanotube pieces as true molecules. The road is Royal not only because it will lead ultimately to continuous fullerene fibers and cables of custom specified composition, but also because the molecular fullerene nanotube pieces themselves, and the technology of modifying and manipulating them, seem likely to spawn major new technologies along the way.

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FINAL PROGRESS REPORT

**Workshop on "Carbon Nanotubes —
Opportunities, Requirements, and Challenges"**

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ONR GRANT N00014-97-1-0664

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For three days at the end of May 1997 nearly 100 scientists, engineers, businessmen, members of the press, and representatives from various government agencies met at Rice University to consider what may be one of the most important new materials to emerge in decades. Perfect tubes made out carbon in the strongest bonding pattern known in nature have now been made in the laboratory. While only a few tens of grams of this material have been produced worldwide, the consensus of the workshop was that both the random tangles of tubes and continuous fibers may ultimately become available at low cost at the level of millions of tons per year. The purpose of the workshop was to consider what can be done to hasten that day, and to consider the technological implications of such an incredible new molecular material.

Carbon nanotubes composed of a single wall of hexagonally-bonded graphene sheet (graphite is made of graphene sheets stacked like pancakes) are members of an infinite family of new all-carbon molecules called "fullerenes." The perfection of the bonding of this graphene membrane gives such fullerene carbon nanotubes wonderful properties:

(1) a tensile strength expected to be higher than any other material, 30-100 times higher than steel at one-sixth the weight;
(2) extreme stiffness combined with ability to withstand repeated bending, buckling, twisting, and/or compression at high rates with complete elasticity;
(3) chemical inertness on the sides of the tube, but facile covalent chemistry available to endlessly modify the tube at the end, regardless of whether they are open or closed;
(4) electrical conduction of a coherent quantum wire, with no Peierls instability; and
(5) thermal conductivity along the tube axis similar to diamond.

While the workshop focussed primarily on these single-walled fullerene nanotubes, it also considered the case where multiple tubular walls are present nested one inside another. Highly imperfect examples of these have been known for decades, produced by the decomposition of hydrocarbons on metal catalyst particles. The high strength "graphite" carbon fibers available commercially for many years, and extensively used to produce high strength composites are distant cousins of the new fullerene tubes. In neither of these cases does the hexagonal carbon network structure extend perfectly along the length. Since it is the perfection of the graphene sheet that produces the extreme properties listed above, these older-technology carbon fibers only hint at the capabilities of fibers with true "fullerene perfection." To emphasize this revolutionary difference from previously existing carbon fibers and tubes, the terms fullerene nanotube and fullerene fiber are used.

In addition, the workshop considered the corresponding structures prepared from hexagonal boron nitride, and hybrid carbon/boron nitride systems. In many ways boron nitride is a perfect partner with carbon. Both take the form of a hexagonal lattice of exceptional strength, with nearly the same lattice constant and spacing between sheets when they stack one upon another. They have nearly the same Young's modulus, and extremely low coefficient of thermal expansion. But while carbon yields fullerene nanotubes that are metallic or small bandgap semiconductors, boron nitride nanotubes are large gap insulators. A metallic carbon nanotube core with a tubular boron nitride outer layer is therefore expected to be an insulated wire on a molecular scale.

One major outcome of the workshop was the description of several paths of research that may lead to the production of fullerene nanotubes in large quantities. Of these the most ambitious, but almost certainly also the most rewarding was one that came to be called the "Royal Road." The beginning of this road is the production of small amounts (grams) of single walled fullerene nanotubes from one of the current methods. The road progresses by developing methods to purify this material, and then to cut these tubes into short pieces. These pieces are then used effectively as seed crystals from which to grow fullerene nanotubes continuously from a hydrocarbon feed gas with the help of a catalyst particle attached at the "living" end. This path of fullerene nanotube research is the "Royal" road because it requires the development of the high science and technology of manipulating individual fullerene nanotube pieces as true molecules. The road is Royal not only because it will lead ultimately to continuous fullerene fibers and cables of custom specified composition, but also because the

molecular fullerene nanotube pieces themselves, and the technology of modifying and manipulating them, seem likely to spawn major new technologies along the way.

The short lengths of fullerene nanotubes that are the principal vehicles along the Royal Road will be molecules in their own right. Since they are made of carbon, these molecules will ultimately constitute a major new branch of organic chemistry. Typically about the diameter of a DNA double helix, these nanotubes can be derivitized at their ends with essentially any organic or organometallic group known, regardless of whether the end of the tube is closed with a hemifullerene done, or open to expose the highly reactive edges of the graphene walls. Alternatively, one or both ends of the tube can be covalently linked to a surface. Using self-assembly techniques, electrically conductive nanotube membranes will be fabricated on surfaces and used as precisely nano-engineered electrodes for capacitors, batteries, fuel cells, electrolysis devices, and photovoltaics.

Fullerene nanotube molecules will bring electricity to organic chemistry. While conductive molecules have been known in the past, but their conductivity has never been comparable to that of true metals such as copper or gold. With doping their conductivity can be improved, but then one no longer has a good molecule. The material is destroyed by exposure to air or water. Fullerene nanotubes, in contrast, remain good conductors even when exposed to air and moisture in the real world. The groups attached to either end of the tube will communicate with each other by true metallic transport.

Fullerene nanotube chemistry therefore appears to have the potential to bring molecular perfection to electrical engineering. Molecular electronics based on fullerene tubes may become a practical reality.

Longer lengths of these fullerene nanotubes can be thought of as a new sort of synthetic polymer of unprecedented mechanical, electrical, and thermal properties. Their growth from molecular fullerene seeds using a catalyst at the end and a gaseous hydrocarbon feedstock at 600-1000°C was seen at the workshop to be an entirely plausible process, one that could potentially operate at megaton/year quantities. When these fullerene nanotubes are finally available at low cost in large quantities, one principal use will most likely be in composites. Particularly when blended with other polymers and epoxies or incorporated as a block in a copolymer, a vast array of new high performance materials and coatings will be possible.

Continuous fibers and cables composed of $\sim 10^{13}$ parallel fullerene tubes per cm^2 cross-section are the principal destination of the Royal Road. These fibers and cables are expected to be the strongest ever made, and quite possibly the strongest that ever can be made. Since the bonding within the walls of each fullerene tube is the strongest that is known, while the bonding between the tubes is weak, the tubes are expected to slide over one another during flexure, producing a nearly infinitely-laminated cable that is extremely tough. Combined with an expected electrical conductivity similar to copper, and a thermal conductivity near that of diamond, these fullerene cables could have vast applications.

One clear outcome of the workshop was the need for greater quantities of high-quality fullerene nanotube material for research and development. Rice University is responding to this need by establishing a non-profit facility — Tubes@Rice — to make gram amounts of raw fullerene nanotube material, and smaller amounts of highly purified material available to researchers. The aim of this service is to enable investigations into novel technological applications of the type discussed during the workshop.

A complete summary of the workshop will be completed by the end of April, 1998, and posted on the World Wide Web (link from http://cnst.rice.edu/reshome.html).